Regio- and stereoselectivity in the Lewis acid- and NaH-induced reactions of thiocamphor with (R)-2-vinyloxirane

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Abstract: The reaction of the enolizable thioketone (1R,4R)-thiocamphor (=(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptane-2-thione; 1) with (R)-2-vinyloxirane (2) in the presence of a Lewis acid such as SnCl4 or SiO2 in anhydrous CH2Cl2 gave the spirocyclic 1,3-oxathiolane 3 with the vinyl group at C(4'), as well as the isomeric enesulfanyl alcohol 4. In the case of SnCl4, an allylic alcohol 5 was obtained in low yield in addition to 3 and 4 (Scheme 2). Repetition of the reaction in the presence of ZnCl2 yielded two diastereoisomeric 4-vinyl-1,3-oxathiolanes 3 and 7 together with an alcohol 4, and a '1 :2 adduct' 8 (Scheme 3). The reaction of 1 and 2 in the presence of NaH afforded regioselectively two enesulfanyl alcohols 4 and 9, which, in CDCl3 , cyclized smoothly to give the corresponding spirocyclic 1,3-oxathiolanes 3, 10, and 11, respectively (Scheme 4). In the presence of HCl, epimerization of 3 and 10 occurred to yield the corresponding epimers 7 and 11, respectively (Scheme 5). The thio-Claisen rearrangement of 4 in boiling mesitylene led to the allylic alcohol 12, and the analogous [3,3]-sigmatropic rearrangement of the intermediate xanthate 13, which was formed by treatment of the allylic alcohol 9 with CS2 and MeI under basic conditions, occurred already at room temperature to give the dithiocarbonate 14 (Schemes 6 and 7). The presented results show that the Lewis acid-catalyzed as well as the NaH-induced addition of (R)-vinyloxirane (2) to the enolizable thiocamphor (1) proceeds stereoselectively via an SN2-type mechanism, but with different regioselectivity.

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Regio- and Stereoselectivity in the *Lewis* Acid- and NaH-Induced Reactions of Thiocamphor with (*R*)-2-Vinyloxirane

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The reaction of the enolizable thioketone (1*R*,4*R*)-thiocamphor (= (1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptane-2-thione; **1**) with (*R*)-2-vinyloxirane (**2**) in the presence of a *Lewis* acid such as $SnCl_4$ or SiO_2 in anhydrous CH_2Cl_2 gave the spirocyclic 1,3-oxathiolane **3** with the vinyl group at C(4′), as well as the isomeric enesulfanyl alcohol **4**. In the case of $SnCl_4$, an allylic alcohol **5** was obtained in low yield in addition to **3** and **4** (*Scheme 2*). Repetition of the reaction in the presence of $ZnCl_2$ yielded two diastereoisomeric 4-vinyl-1,3-oxathiolanes **3** and **7** together with an alcohol **4**, and a '1:2-adduct' **8** (*Scheme 3*). The reaction of **1** and **2** in the presence of NaH afforded regioselectively two enesulfanyl alcohols **4** and **9**, which, in $CDCl_3$, cyclized smoothly to give the corresponding spirocyclic 1,3-oxathiolanes **3**, **10** and **11**, respectively (*Scheme 4*). In the presence of HCl, epimerization of **3** and **10** occurred to yield the corresponding epimers **7** and **11**, respectively (*Scheme 5*). The thio-*Claisen* rearrangement of **4** in boiling mesitylene led to the allylic alcohol **12**, and the analogous [3,3]-sigmatropic rearrangement of the intermediate xanthate **13**, which was formed by treatment of the allylic alcohol **9** with CS_2 and MeI under basic conditions, occurred already at room temperature to give the dithiocarbonate **14** (*Schemes 6 and 7*). The presented results show that the *Lewis* acid-catalyzed as well as the NaH-induced addition of (*R*)-vinyloxirane (**2**) to the enolizable thiocamphor (**1**) proceeds stereoselectively *via* an S_N2-type mechanism, but with different regioselectivity.

1. Introduction. – 1,3-Oxathiolanes can be prepared by the *Lewis* acid-catalyzed reaction of oxiranes not only with non-enolizable and enolizable thioketones, but with enolized thioketones as well [1 – 8]. The latter reaction occurs in two steps *via* an intermediate enesulfanyl alcohol [6]. In the cases of (*R*)-2-phenyl- and (*R*)-2-vinyloxirane, the reactions proceed with high regio- and stereoselectivity *via* an S_N2-type mechanism (*Scheme 1*): the nucleophilic thiocarbonyl S-atom attacks preferentially at C(2) of the *Lewis* acid activated oxiranes, leading to the 'direct' or 'indirect' formation of 4-substituted 1,3-oxathiolanes with inversion of the configuration.

Scheme 1

Enolizable thioketones exist predominantly in the enethiol form [9] [10], which can be deprotonated with a strong base such as NaH. The formed thioanion can cleave the 3-membered ring of oxiranes *via* an analogous S_N2-type mechanism as under *Lewis* acid catalysis, but the regioselectivity is different. The reactions afford enesulfanyl alcohols, which cyclize smoothly to give the corresponding ring-enlarged 1,3-oxathiolanes as well [5] [6].

In the present paper, the results of the reaction of (1*R*,4*R*)-thiocamphor (= (1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptane-2-thione; **1**) with (*R*)-2-vinyloxirane (**2**) in the presence of *Lewis* acids and of NaH, respectively, are described.

2. Results. – 2.1. *Reaction of (1*R*,4*R*)-Thiocamphor* (**1**) *with (R)-2-Vinyloxirane* (**2**). On dropping two equiv. of **2** into a solution of **1** and 0.5 equiv. of $SnCl_4$ in anhydrous CH_2Cl_2 at – 78° during 20 min under an N_2 atmosphere, the color of the yellow solution turned slowly to light yellow. After stirring the reaction mixture for an additional 5 min, the reaction was quenched by addition of

a saturated aqueous $NaHCO_3$ solution. Chromatographic separation of the mixture gave the spirocyclic 1,3-oxathiolane **3**, the enesulfanyl alcohol **4**, and camphor (**6**) in 49, 23, and 2% yield, respectively, as well as an unexpected alcohol **5** in 3% yield. Repetition of the reaction with silica gel as catalyst at 0° for 2 d led to **3**, **4**, and **6** in 39, 6, and 1% yield, respectively, but no alcohol **5** was observed. In both cases, the reaction was almost complete and the starting material **1** was recovered only in a small amount (*Scheme 2* and *Table 1*).

Scheme 2

Table 1

The reaction of **1** and **2** in a ratio of 1:2 was also repeated in the presence of 0.5 equiv. of $ZnCl_2$ under an N_2 atmosphere at – 30° for 5 h, and the mixture was kept at – 20° for 18 h. Chromatographic separation of the mixture afforded two diastereoisomeric spirocyclic 1,3-oxathiolanes **3** and **7**, and the alcohol **4** in 16, 32, and 4% yield, respectively, as well as another unexpected product **8** in 13% yield (*Scheme 3*). The latter contains two vinyl groups, indicating that two molecules of **2** have reacted, but there are also two S-atoms in **8**.

Scheme 3

The structures of **3**, **4**, **7**, and **8** were assigned on the basis of their elemental analyses, ^{1}H-, ^{13}C-, 2D-NMR-, and mass spectra, and by comparison with those of similar compounds described previously [3 – 7]. The configurations at C(2) and C(4′) of **3** and **7** were determined by means of NOESY spectra relative to the known absolute configuration of the bicyclic skeleton of thiocamphor (**1**). The

examination of a *Dreiding* model of **3** shows that the spatial distance between the methine H-atom of the vinyl group and the Me–C(1) group is small, in good agreement with the NOESY spectrum (500 MHz, $CDCl_3$) of **3**, which shows one relevant cross-signal between C*H*=CH_2 at 5.82 ppm and Me–C(1) at 0.99 ppm. It is worth mentioning that the difference between the chemical shifts of H_{endo}–C(6) at 2.15–2.10 ppm and H_{exo}–C(6) at 1.51–1.45 ppm is ($\Delta\delta$) ≈ 0.65 ppm due to the proximity of the electronegative O-atom, which means that the O-atom is close to H_{endo}–C(6), *i.e.*, in the *endo* position (*cf.* [6]). These analyses indicate that the absolute configuration of **3** is (1*R*,2*R*,4*R*,4′*S*). Similarly, the NOESY spectrum of **7** (500 MHz, $CDCl_3$) shows one relevant cross-signal between H–C(4′) at 3.95–3.90 ppm and Me–C(1) at 0.91 ppm, but the signals of H_{endo}–C(6) and H_{exo}–C(6) overlap at 1.57–1.54 ppm, which implies that the O-atom is *exo*-oriented. Therefore, it can be deduced that **7** possesses the (1*R*,2*S*,4*R*,4′*S*) configuration, *i.e.*, it is the C(2) epimer of **3**.

The absolute configuration at C(2) in **4** has been assigned based on the knowledge that ring opening of (*R*)-2-vinyloxirane (**2**) takes place *via* nucleophilic attack at C(2) and the cleavage of the O–C(2) bond occurs under inversion of the configuration at C(2) [7]. The structure of compound **5**, *i.e.*, the product of a thio-*Claisen* rearrangement followed by dethionation (*cf.* [11] [12]), was proposed on the basis of its CI-MS, ^{1}H-NMR, and IR spectrum. The latter shows an intensive carbonyl absorption at 1739 cm^{-1} and a broad absorption for OH at 3425 cm^{-1}. In the ^{1}H-NMR spectrum, multiplets for two olefinic H-atoms (5.8–5.2 ppm) and a CH_2O-group (4.15–4.05 ppm) are characteristic. Furthermore, a set of 6 Me signals indicate a mixture of two isomers. The formation of **8** and its configuration will be discussed in *Section 3*.

2.2. *Reaction of* **1** *and* **2** *in the Presence of NaH.* To a solution of **1** in anhydrous THF, 1.2 equiv. of NaH were poured at room temperature. After

stirring the mixture for 30 min, 1.3 equiv. of **2** were added dropwise. The reaction was followed by TLC and was completed after 6 h. Chromatographic separation of the mixture gave the secondary alcohol **9** and the primary alcohol **4** in 70 and 22% yield, respectively (*Scheme 4*).

Scheme 4

The formation of **4** and **9** proceeded *via* nucleophilic attack of the enethiolate, which is formed by deprotonation of the starting material **1**, at C(2) and C(3) of (*R*)-2-vinyloxirane (**2**), leading to **4** and **9** with inversion and retention of the configuration at C(2), respectively. This proposal was proven by the structures of the cyclization products **3**, **10**, and **11**.

In $CDCl_3$ at room temperature, the primary alcohol **4** cyclized quantitatively to give the 4-vinyl substituted 1,3-oxathiolane **3**. The cyclization of the secondary alcohol **9** occurred also smoothly under the same conditions, leading to a mixture of the 5-vinyl substituted 1,3-oxathiolanes **10** and **11** in 86 and 14% yield, respectively (ratio 6.1:1, *Scheme 4*). Treatment of **9** with one equiv. of $ZnCl_2$ in boiling THF under an N_2 atmosphere for 2 h gave 47% of **10** and 36% of **11** (ratio of 1.3:1).

Again, the structures of **9**, **10**, and **11** were assigned on the basis of their elemental analyses and spectroscopic data and by comparison with compounds described previously (see [3 – 7] and *Sect. 2.1*). The configurations of the spirocyclic 1,3-oxathiolanes **10** and **11** were determined by means of NOESY-spectra, relative to the known absolute configuration of the bicyclic skeleton of the starting material **1**: the examination of a *Dreiding* model of **10** shows that the spatial distance between the methine H-atom of the vinyl group and the Me–C(1) group is small, in agreement with the NOESY spectrum (600 MHz, $CDCl_3$) of **10**,

which shows one cross-signal between C*H*=CH_2 at 5.92 ppm and Me–C(1) at 0.94 ppm, as well as two relevant cross-signals between H–C(5′) at 4.32–4.28 ppm and H_{exo}–C(3) at 2.37 ppm and H_{endo}–C(3) at 1.75–1.73 ppm. In addition, $\Delta\delta$ of H_{endo}–C(6) at 2.17 ppm and H_{exo}–C(6) at 1.44 ppm is 0.73 ppm, which demonstrates that the O-atom is close to H_{endo}–C(6), *i.e.*, the O-atom is in the *endo*-position. Therefore, **10** has the (1*R*,2*R*,4*R*,5′*R*) configuration. The NOESY spectrum of **11** (600 MHz, $CDCl_3$) shows one relevant cross-signal between H–C(5′) at 4.52–4.49 ppm and Me–C(1) at 0.92 ppm, and the signals of H_{endo}–C(6) and H_{exo}–C(6) overlap at 1.57–1.46 ppm, indicative for an *exo*-oriented O-atom. Therefore, **11** is the C(2) epimer of **10** with the absolute configuration (1*R*,2*S*,4*R*,5′*R*).

2.3. *Epimerization of* **3** *and* **10**. Irradiation of a $CDCl_3$-solution of **3** in an NMR-tube with sunlight at room temperature for 16 h afforded a mixture of **3** and **7** in a ratio of 1:15. Treatment of **3** with one equiv. of $ZnCl_2$ in boiling THF under an N_2 atmosphere for 45 min led to a 1:1 mixture of **3** and **7** according to an ^{1}H-NMR analysis (*Scheme 5*). However, no epimerization of **3** took place when it was treated with 0.5 equiv. of $ZnCl_2$ in CH_2Cl_2 at – 20° for 26 h.

Treatment of a solution of **10** in $CHCl_3$ at room temperature with 10 drops of conc. HCl for 14 h yielded 42% of **11**, and 40% of the starting material **10** was recovered (*Scheme 5*).

Scheme 5

2.4. *Thio*-Claisen *Rearrangement of* **4**. As it was proposed that the minor product **5** (*Scheme 2*) is the product of a [3,3]-sigmatropic rearrangement (thio-*Claisen* rearrangement [11] [12]) of **4** and subsequent dethionation, we examined the thermolysis of **4**. Heating of a solution of **4** in mesitylene to reflux under an N_2 atmosphere for 12 min yielded stereospecifically **12** as a pink orange oil in 88%

yield (*Scheme 6*). Treatment of **4** in the presence of $ZnCl_2$ in CH_2Cl_2 under an N_2 atmosphere at – 30° for 3 h gave **5** in 30% yield[2]).

Scheme 6

The structure of **12** was assigned as in the previous cases. The NOESY spectrum (500 MHz, $CDCl_3$) shows one relevant cross-peak between H–C(3) at 2.67–2.63 ppm and Me_{syn}–C(7) at 0.82 ppm. Furthermore, there are two relevant cross-signals between 2 H–C(4′) of the side chain at 4.13–4.07 ppm and 2 H–C(1′) at 2.04–1.98 ppm and the H-atom of the OH group at 1.56–1.49 ppm, confirming the (*Z*)-configuration. In addition, H_{exo}–C(3) appeared as a multiplet instead of a *ddd*-signal due to the *w*-coupling with H_{exo}–C(5). These analyses indicate an *endo*-oriented side-chain at C(3) and an absolute configuration of (1*R*,2*S*,4*R*,2′*Z*).

2.5. *[3,3]-Sigmatropic Rearrangement of Intermediate Xanthate* **13**. A mixture of **9** and five equiv. of MeI in a two-phase system of 50% aq. NaOH containing 0.1 equiv. of *n*-Bu_4NHSO_4 and 2.2 ml of CS_2 was vigorously stirred overnight at room temperature. After separation of the CS_2 layer and workup, dithiocarbonate **14** was obtained as a yellow oil in 81% yield (*Scheme 7*). We propose that **14** was formed *via* a [3,3]-sigmatropic rearrangement of the intermediate xanthate **13**.

Scheme 7

The structure of **14** was assigned on the basis of its NMR and mass spectra. The configuration of the side-chain double bond of **14** was determined by means of 1D-NOESY and IR spectrum. The 1D-NOESY spectrum (300 MHz, $CDCl_3$),

[2]) Unfortunately, this reaction was found to be non-reproducible.

on irradiation of 2 H–C(1) at 3.62 ppm, showed no NOE signal for 2 H–C(4) at 3.27 ppm, and *vice versa*. In the IR spectrum of **14**, a strong absorption band at 963 cm^{-1} is indicative for the (2*E*)-configuration[3]).

3. Discussion and Conclusion. – The results presented show that 1,3-oxathiolanes can be prepared not only by the *Lewis* acid catalyzed reaction of an enolizable thioketone with 2-vinyloxirane, but also under basic conditions. Thiocamphor (**1**) reacts with (*R*)-vinyloxirane (**2**) in the presence of a *Lewis* acid to yield spirocyclic 1,3-oxathiolanes **3** and **7**, as well as the enesulfanyl alcohol **4**, with high regio- and stereoselectivity (*Schemes 2* and *3*). The reaction proceeds *via* an S_N2-type mechanism, whereby the nucleophilic thiocarbonyl S-atom preferentially attacks the more hindered C(2)-atom of the activated **2** (O–C(2) cleavage), leading to products with inversion of the configuration, in analogy to the reaction of **1** with (*R*)-2-phenyloxirane [5].

In contrast, the reaction of thiocamphor (**1**) with **2** under basic conditions, *i.e.*, the reaction of the enethiolate anion with **2**, afforded two enesulfanyl alcohols **4** and **9** with low regioselectivity (*Scheme 4*). We propose that this reaction proceeds also *via* an S_N2-type mechanism, in which the preferred nucleophilic attack of the enethiolate anion occurs at C(3) (O–C(3) cleavage) to give **9** with retention of the configuration, whereas the formation of the minor product **4** takes place *via* O–C(2) cleavage with inversion of the configuration at C(2) of the oxirane **2**.

The enesulfanyl alcohols **4** and **9** isomerize smoothly *via* the mechanism reported previously [5] to give the corresponding spirocyclic 1,3-oxathiolanes in the presence of traces of DCl that is formed during the storage of $CDCl_3$ (*Scheme 4*). The observed epimerizations at the spiro-centre in the cases of **3/7** and **10/11**

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[3]) In addition, the (2*E*)-configuration was supported by a computer simulation of the ^{1}H-NMR spectrum [13].

(*Scheme 5*) can be explained by the mechanism described earlier [5], *i.e.*, an acid-catalyzed ring-opening/ring-closure reaction of the S/O-acetal.

A likely mechanism of the formation of adduct **8** is proposed in *Scheme 8*. The $ZnCl_2$-catalyzed reaction of **1** and **2** leads to two spirocyclic diastereoisomers **3** and **7**, which then decompose to give camphor **6** and (*S*)-2-vinylthiirane (**15**) *via* the ring-opening of the 1,3-oxathiolanes and the subsequent nucleophilic attack of the S-atom at C(5′). The analogous decomposition reaction of 1,3-oxathiolanes in the presence of *Lewis* acids was described in the previous work [1] [14]. Then, the thiirane ring is cleaved by nucleophilic attack of the S-atom of **1** at the less hindered C(3)-atom (S–C(3) cleavage) of **15** with retention of the configuration at C(2) of **15**, which leads to the intermediate enesulfanyl thiol **16**. Finally, O–C(2) cleavage of oxirane **2** by nucleophilic attack of the SH group of **16** with inversion of configuration affords the unexpected adduct **8**. As a result of this reaction mechanism, we propose that the configuration of **8** is (*S*,*S*). This cascade reaction demonstrates the influence of the heteroatom upon the regioselectivity of the ring-opening of 3-membered rings. In contrast to oxiranes, the ring-opening of thiirane **15** proceeds *via* nucleophilic attack of the thiocarbonyl S-atom at the less hindered C(3)-atom (S–C(3) cleavage). Because the difference of the electronegativities of S- and C-atom is small, the partial positive charges at C(2) and C(3) of thiiranes are much lower than those of oxiranes, so that the steric hindrance dominates the ring-opening of thiiranes in favour of the S–C(3) cleavage (*Scheme 8*).

Scheme 8

The rearrangement of allylic xanthates is known to proceed thermally (*ca.* 100°) *via* a concerted reaction mechanism ([3,3]-sigmatropic rearrangement) [15]. It can be accelerated by catalysis with *β*-cyclodextrin, in which case the reaction

occurs in an inclusion complex at 2-5° [16]. The formation of the dithiocarbonate **14** *via* the intermediate **13** occurs stereospecifically and smoothly *in situ* at room temperature. A concerted mechanism, *i.e.*, a [3,3]-sigmatropic rearrangement is postulated *via* the transition state **A**, in which a neighboring group participation is responsible for the acceleration of the reaction (*Scheme 9*).

Scheme 9

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Experimental Part

1. *General*. See [7] [17]. Optical rotations were recorded on a *Perkin-Elmer-241* polarimeter (c = 1, in THF). IR Spectra: film, cm^{-1}. NMR Spectra: at 500 or 600 (^1H) and 125.8 or 150.9 MHz (^{13}C) in $CDCl_3$ or C_6D_6 if not otherwise stated. Assignment of signals based on 2D NMR spectra.

2. *General Procedures for the Reactions of (1*R*,4*R*)-Thiocamphor* (= (1*R*,4*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptane-2-thione; **1**) *with (*R*)-2-Vinyloxirane* (**2**). *General Procedure 1* (*GP1*): To a soln. of **1** (*ca.* 1 mmol) in anh. CH_2Cl_2 (10 – 15 ml) under N_2 atmosphere, $SnCl_4$ (0.5 equiv.) was added at – 78°. This led to little change in the color of the soln. After stirring the mixture for 15 min at – 78°, *ca.* 2 equiv. of **2** were added dropwise within 20 min, whereby the color of the soln. changed to pale yellow. After stirring the mixture for an additional 5 min, the

reaction was quenched by addition of H_2O, and the mixture was washed with sat. aq. NaCl soln. (3×). The combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo*. The products were separated by chromatography (SiO_2; hexane/Et_2O; CC or prep. TLC (PLC)).

General Procedure 2 (*GP2*): To a soln. of **1** (*ca.* 1 mmol) and **2** (*ca.* 2 mmol) in anh. CH_2Cl_2 (10 – 15 ml) under an N_2 atmosphere, 4.5 g of silica gel were added at r.t. After stirring the suspension for 2 d at 0°, the mixture was filtered, and the residue was washed with Et_2O (4×). Then, the combined filtrate was evaporated *in vacuo*. The products were separated as in *GP1*.

General Procedure 3 (*GP3*): To a soln. of **1** (*ca.* 2 mmol) in anh. CH_2Cl_2 (15 ml) under N_2 atmosphere, 0.5 equiv. of $ZnCl_2$ was added at – 30°. After stirring the mixture for 15 min at – 30°, *ca.* 2 equiv. of **2** were added dropwise. Then, the mixture was stirred for 5 h at – 30°, kept for 18 h at – 20°, and the reaction was quenched by addition of H_2O. The mixture was washed with sat. aq. NaCl soln. (3×). The combined org. layers were dried ($MgSO_4$) and evaporated *in vacuo*. The products were separated by CC (SiO_2; hexane/Et_2O).

General Procedure 4 (*GP4*)*:* To the soln. of **1** (*ca.* 5 mmol) in anh. THF (25 ml), 1.2 equiv. of NaH (95% purity) were added at 25°. After stirring the mixture for 30 min, 1.3 equiv. of **2** were added dropwise to the almost colorless solution. The reaction was controlled by TLC and was completed after 6 h. After aq. work-up, the products were separated by CC (SiO_2; hexane/Et_2O).

3. *Reactions of* **1** *with (*R*)-2-Vinyloxirane* (**2**). 3.1. Lewis *Acid-Catalyzed Reaction of* **1** *and* **2**. Reaction of **1** (168 mg, 1 mmol) with **2** (140 mg, 2 mmol) and 0.5 equiv. of $SnCl_4$ (or 4.5 g of SiO_2) at – 78 ° or 0° (CC, prep. TLC (PLC) hexane/Et_2O) according to *GP1* yielded 117 mg (49%) (or 93 mg, 39%) of *(1*R*,2*R*,4*R*,4'*S*)-1,7,7-trimethyl-4'-vinylspiro[bicyclo[2.2.1]heptane-2,2'-[1,3]oxathiolane]* (**3**), 55 mg (23%) (or 15 mg, 6%) of *(2*S*)-2-[(1'*R*,4'*R*)-(1',7',7'-*

trimethylbicyclo[2.2.1]hept-2′-en-2′-yl)sulfanyl]but-3-en-1-ol (**4**), 7 mg (3%) of *(1*R*,3*S*,4*R*)-3-((2*Z*)-4′-hydroxybut-2′-en-1′-yl)-1,7,7-trimethylbicyclo[2.2.1]-heptane-2-one* (**5**) and 2 mg (1%) of camphor (**6**) (*Table 1*).

Data of **3**: Colorless oil. $[\alpha]_D^{23}$ = – 146.8. IR: 3081*w*, 2954*s*, 2869*m*, 1636*m*, 1476*m*, 1453*m*, 1418*w*, 1389*m*, 1372*m*, 1305*w*, 1272*w*, 1250*w*, 1194*w*, 1113*m*, 1083*s*, 1044*m*, 1017*m*, 987*m*, 958*w*, 914*m*, 882*m*, 819*m*, 809*m*, 701*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.82 (*ddd*, *J* = 16.9, 9.9, 7.9, C*H*=CH_2); 5.10 (*ddd*, *J* = 17.0, 1.4, 0.9, 1 H of =CH_2); 4.97 (*ddd*, *J* = 9.8, 1.4, 0.5, 1 H of =CH_2); 4.02–3.98 (*m*, H–C(4′)); 3.96 (*dd*, *J* = 9.2, 2.5, 1 H–C(5′)); 3.87 (*dd*, *J* = 9.2, 5.2, 1 H–C(5′)); 2.37 (*ddd*, *J* = 13.9, 4.7, 3.2, H_{exo}–C(3)); 2.15–2.10 (*m*, H_{endo}–C(6)); 1.74–1.67 (*m*, H–C(4), H_{exo}–C(5)); 1.70 (*d*, *J* = 13.8, H_{endo}–C(3)); 1.51–1.45 (*m*, H_{exo}–C(6)); 1.26–1.20 (*m*, H_{endo}–C(5)); 0.99 (*s*, Me–C(1)); 0.93 (*s*, Me_{syn}); 0.88 (*s*, Me_{anti}). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 138.8 (*d*, *C*H=CH_2); 114.5 (*t*, CH=*C*H_2); 105.1 (*s*, C(2)); 73.6 (*t*, C(5′)); 53.9(*s*, C(1)); 52.6 (*d*, C(4′)); 50.1 (*t*, C(3)); 48.5 (*s*, C(7)); 46.2 (*d*, C(4)); 30.2 (*t*, C(6)); 27.4 (*t*, C(5)); 21.0 (*q*, Me_{syn}), 20.2 (*q*, Me_{anti}); 14.1 (*q*, Me–C(1)). ESI-MS (MeOH + NaI): 277 (28, $[M + K]^+$), 263 (14), 262 (18), 261 (100, $[M + Na]^+$), 245 (24), 229 (7), 207 (11). Anal. calc. for $C_{14}H_{22}OS$ (238.39): C 70.54, H 9.30; found C 70.24, H 9.16.

Data of **4**: Colorless oil. $[\alpha]_D^{23}$ = + 0.27. IR: 3375*m* (br., OH), 3083*w*, 2984*m*, 2953*s*, 2871*m*, 1637*w*, 1561*w*, 1472*w*, 1456*w*, 1440*w*, 1416*w*, 1385*m*, 1375*w*, 1365*w*, 1297*w*, 1184*w*, 1134*w*, 1106*m*, 1062*m*, 1043*m*, 1025*m*, 983*m*, 921*m*, 875*w*, 819*w*, 783*w*, 715*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.88–5.77 (*m*, H–C(3)); 5.73 (*d*, *J* = 3.3, H–C(3′)); 5.33 (*d*, *J* = 17.1, 1 H–C(4)); 5.25 (*d*, *J* = 10.9, 1 H–C(4)); 3.71–3.65 (*m*, 2 H–C(1), H–C(2)); 2.36 (*t*, *J* = 3.5, H–C(4′)); 1.93–1.83 (*m*, OH, H_{exo}–C(5′)); 1.55–1.45 (*m*, H_{exo}–C(6′)); 1.10–0.96 (*m*, H_{endo}–C(5′), H_{endo}–C(6′)); 1.01 (*s*, Me–C(1)); 0.81 (*s*, Me_{syn}); 0.78 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 141.2 (*s*, C(2′)); 135.2 (*d*, C(3)); 128.8 (*d*, C(3′)); 118.2 (*t*, C(4)); 63.8 (*t*,

C(1)); 56.8 (*s*, C(1′)); 56.0 (*s*, C(7′)); 52.3 (*d*, C(4′)); 50.5 (*d*, C(2)); 31.5 (*t*, C(6′)); 26.3 (*t*, C(5′)); 19.6 (*q*, Me_{anti}); 19.4 (*q*, Me_{syn}); 11.4 (*q*, Me–C(1)). CI-MS (NH_3): 241 (6), 240 (16), 239 (100, $[M + H]^+$), 221 (7), 169 (5).

Data of **5**: Colorless oil. IR (film): 3425*m* (br.), 2960*s*, 2873*m*, 1739*s*, 1447*m*, 1392*m*, 1372*m*, 1324*w*, 1093*m*, 1016*m*, 971*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.80–5.60 (*m*, 2 H); 4.15–4.05 (*m*, CH_2O); 2.65–2.40 (*m*, *ca.* 1 H); 2.10–1.85 (*m*, *ca.* 3 H); 1.80-1.25 (*m*, *ca.* 4 H); 0.93, 0.87, 0.84, 0.83, 0.80, 0.78 (6 *s*, 3 Me). CI-MS (NH_3): 240 (28, $[M + NH_4]^+$), 206 (16), 205 (100, $[M - H_2O + H]^+$).

Repetition of the reaction of **1** (336 mg, 2 mmol), **2** (280 mg, 4 mmol) and 0.5 equiv. of $ZnCl_2$ according to *GP3* afforded 52 mg (11%) of **3**, 176 mg (37%) of *(1*R*,2*S*,4*R*,4′*S*)-1,7,7-trimethyl-4′-vinylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**7**), 9.5 mg (4%) of **4**, and 84.2 mg (13%) of *(2*S*)-2-[1′-(1′*S*)-({[((1′*R*,4′*R*)-1″,7″,7″-trimethylbicyclo[2.2.1]hept-2″-en-2″-yl)sulfanyl]methyl}prop-2′-en-1′-yl)sulfanyl]but-3-en-1-ol* (**8**).

Data of **7**: Colorless oil. $[\alpha]_D^{23}$ = – 131.1. IR: 3083*w*, 2956*s*, 2884*m*, 1636*w*, 1480*m*, 1453*m*, 1417*w*, 1389*m*, 1370*m*, 1306*w*, 1248*w*, 1201*w*, 1161*w*, 1138*w*, 1110*m*, 1086*s*, 1052*m*, 1016*w*, 986*m*, 943*w*, 917*m*, 873*w*, 837*m*, 804*w*, 736*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.74 (*ddd*, *J* = 16.9, 9.9, 7.9, C*H*=CH_2); 5.19 (*dd*, *J* = 16.9, 1.3, 1 H of =CH_2); 5.05 (*dd*, *J* = 9.8, 1.2, 1 H of =CH_2); 4.19 (*dd*, *J* = 9.3, 5.9, 1 H–C(5′)); 3.95–3.90 (*m*, H–C(4′)); 3.66 (*dd*, *J* = 9.2, 8.2, 1 H–C(5′)); 2.37 (*ddd*, *J* = 13.5, 4.5, 3.2, H_{exo}–C(3)); 2.00 (*d*, *J* = 13.5, H_{endo}–C(3)); 1.77 (*t*, *J* = 4.5, H–C(4)); 1.75–1.67 (*m*, H_{exo}–C(5)); 1.57–1.54 (*m*, 2 H–C(6)); 1.23–1.18 (*m*, H_{endo}–C(5)); 1.01 (*s*, Me_{syn}); 0.91 (*s*, Me–C(1)); 0.87 (*s*, Me_{anti}). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 136.5 (*d*, *C*H=CH_2); 116.8 (*t*, CH=*C*H_2); 106.9 (*s*, C(2)); 74.7 (*t*, C(5′)); 53.8(*s*, C(1)); 51.7 (*d*, C(4′)); 51.6 (*t*, C(3)); 48.3 (*s*, C(7)); 45.9 (*d*, C(4)); 34.7 (*t*, C(6)); 27.1 (*t*, C(5)); 21.1 (*q*, Me_{anti}); 20.7 (*q*, Me_{syn}); 10.0 (*q*, Me–C(1)). ESI-MS (MeOH + NaI): 278 (18), 277 (83, $[M + K]^+$), 261 (25, $[M + Na]^+$), 229

(7), 207 (7), 173 (14). Anal. calc. for $C_{14}H_{22}OS$ (238.39): C 70.54, H 9.30, S 13.45; found C 70.40, H 9.18, S 13.57.

Data of **8**: Colorless oil. $[\alpha]_D^{23}$ = + 30. IR: 3406*m* (br., OH), 3081*w*, 2953*s*, 2870*m*, 1635*w*, 1561*w*, 1456*m*, 1416*m*, 1386*m*, 1296*m*, 1068*m*, 1042*m*, 985*m*, 918*m*, 794*w*, 715*w*. ^{1}H-NMR (600 MHz, C_6D_6): 5.64 (*ddd*, *J* = 17.0, 10.1, 8.5, H–C(2′)); 5.60 (*d*, *J* = 3.3, H–C(3″)); 5.54 (*ddd*, *J* = 17.2, 10.2, 8.5, H–C(3)); 5.04 (*dt*-like, *J* ≈ 17.0, 2.1, 1 H–C(3′)); 4.96–4.90 (*m*, 2 H–C(4), 1 H–C(3′)); 3.64 (*ddd*, *J* = 8.9, 8.6, 5.2, H–C(1′)); 3.46 (br. *m*, 2 H–C(1)); 3.21–3.17 (*m*, H–C(2)); 2.84 (*dd*, *J* = 13.1, 5.1, 1 H of CH_2S); 2.63 (*dd*, *J* = 13.1, 9.1, 1 H of CH_2S); 2.26 (*t*, *J* = 3.4, H–C(4″)); 1.81–1.76 (*m*, H_{exo}–C(5″)); 1.53 (br. *m*, OH); 1.43 (*ddd*, *J* = 12.0, 5.2, 3.5, H_{exo}–C(6″)); 1.16 (*ddd*, *J* = 11.9, 5.5, 3.8, H_{endo}–C(6″)); 1.08 (*s*, Me–C(1″)); 0.99 (*ddd*, *J* = 11.6, 5.9, 3.5, H_{endo}–C(5″)); 0.92 (*s*, Me_{syn}); 0.69 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, C_6D_6): 142.8 (*s*, C(2″)); 137.6 (*d*, C(3)); 136.8 (*d*, C(2′)); 128.4 (*d*, C(3"), assigned by means of HSQC and HSQC-TOCSY spectra); 117.5 (*t*, C(4)); 117.2 (*t*, C(3′)); 64.4 (*t*, C(1)); 57.4 (*s*, C(1″)); 56.3 (*s*, C(7″)); 53.1 (*d*, C(4″)); 52.8 (*d*, C(2)); 49.0 (*d*, C(1′)); 34.9 (*t*, *C*H_2S); 31.9 (*t*, C(6″)); 27.4 (*t*, C(5″)); 20.1 (*q*, Me_{anti}, Me_{syn}); 12.0 (*q*, Me–C(1″)). CI-MS (NH_3): 327 (10), 326 (19), 325 (87, $[M + H]^+$), 221 (15), 169 (11), 159 (10), 157 (100).

3.2. *NaH-Activated Reaction of* **1** *and* **2**. Reaction of **1** (840 mg, 5 mmol), NaH (151 mg, 6.3 mmol) and **2** (455 mg, 6.5 mmol) in anh. THF at r.t. (6 h, CC, hexane/Et_2O) according to *GP4* gave 830 mg (70%) of *(2*R*)-1-[(1*′R*,4*′R*)-(1′,7′,7′-trimethylbicyclo[2.2.1]hept-2′-en-2′-yl)sulfanyl]but-3-en-2-ol* (**9**) and 260 mg (22%) of **4**.

Data of **9**: Colorless oil. $[\alpha]_D^{23}$ = + 2.76. IR: 3382*m* (br., OH), 3081*w*, 3059*w*, 2984*m*, 2953*s*, 2871*m*, 1644*w*, 1561*m*, 1471*m*, 1452*m*, 1440*m*, 1420*m*, 1385*m*, 1375*m*, 1365*m*, 1297*m*, 1290*m*, 1279*m*, 1254*w*, 1185*w*, 1106*m*, 1045*m*, 985*m*, 925*m*, 875*w*, 820*w*, 781*w*, 714*w*. ^{1}H-NMR (600 MHz, C_6D_6): 5.73 (*ddd*, *J* = 17.1,

10.5, 5.5, H–C(3)); 5.43 (*d*, *J* = 3.4, H–C(3′)); 5.23 (*dt*-like, *J* ≈ 17.2, 1.5, 1 H–C(4)); 4.98 (*dt*-like, *J* ≈ 10.5, 1.5, 1 H–C(4)); 4.12–4.09 (*m*, H–C(2)); 2.68 (*dd*, *J* = 13.3, 4.5, 1 H–C(1)); 2.57 (*dd*, *J* = 13.3, 8.0, 1 H–C(1)); 2.23 (*t*, *J* = 3.5, H–C(4′)); 1.92 (*d*, *J* = 3.8, OH); 1.81–1.76 (*m*, H_{exo}–C(5′)); 1.43 (*ddd*, *J* = 12.1, 5.2, 3.5, H_{exo}–C(6′)); 1.15 (*ddd*, *J* = 12.1, 5.4, 3.8, H_{endo}–C(6′)); 1.06 (*s*, Me–C(1)); 0.98 (*ddd*, *J* = 12.3, 5.7, 3.6, H_{endo}–C(5′)); 0.88 (*s*, Me_{syn}); 0.68 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, C_6D_6): 144.3 (*s*, C(2′)); 139.9 (*d*, C(3)); 125.7 (*d*, C(3′)); 115.5 (*t*, C(4)); 70.8 (*d*, C(2)); 57.2 (*s*, C(1′)); 56.6 (*s*, C(7′)); 52.8 (*d*, C(4′)); 39.1(*t*, C(1)); 32.2 (*t*, C(6′)); 27.3 (*t*, C(5′)); 20.08, 20.05 (2*q*, Me_{anti}, Me_{syn}); 11.9 (*q*, Me–C(1)). CI-MS (NH_3): 241(6), 240 (16), 239 (100, $[M + H]^+$). Anal. calc. for $C_{14}H_{22}OS$ (238.39): C 70.54, H 9.30, S 13.45 ; found C 70.20, H 9.14, S 13.41.

4. *Isomerization of* **4** *to* **3***, and of* **9** *to* **10** *and* **11**. The cyclization of **4** (*ca.* 15 mg) to **3** proceeded quantitatively in $CDCl_3$ (0.5 ml, NMR-tube) in 15 min at r.t. The cyclization of **9** (50 mg) under the same conditions (10 min) led to 86% of *(1*R*,2*R*,4*R*,5′*R*)-1,7,7-trimethyl-5′-vinylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**10**) and 14% of *(1*R*,2*S*,4*R*,5′*R*)-1,7,7-trimethyl-5′-vinylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]oxathiolane]* (**11**).

Data of **10**: Colorless oil. $[\alpha]_D^{23}$ = – 27.1. IR: 3083*w*, 2985*s*, 2952*s*, 2873*s*, 1647*w*, 1477*m*, 1453*m*, 1389*m*, 1371*w*, 1318*w*, 1272*w*, 1195*w*, 1159*w*, 1113*m*, 1071*s*, 1027*m*, 1003*w*, 986*m*, 960*w*, 925*m*, 887*w*, 834*w*, 808*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.92 (*ddd*, *J* = 17.3, 10.5, 6.4, C*H*=CH_2); 5.38 (*dd*, *J* = 17.3, 1.3, 1 H of =CH_2); 5.21 (*dd*, *J* = 10.5, 1.3, 1 H of =CH_2); 4.32–4.28 (*m*, H–C(5′)); 2.94 (*dd*, *J* = 10.0, 4.5, 1 H–C(4′)); 2.50 (*t*-like, *J* ≈ 10.2, 1 H–C(4′)); 2.37 (*ddd*, *J* = 13.9, 4.8, 3.1, H_{exo}–C(3)); 2.17 (*ddd*, *J* = 13.1, 5.5, 3.7, H_{endo}–C(6)); 1.75–1.73 (*m*, H_{endo}–C(3), H–C(4)); 1.72–1.66 (*m*, H_{exo}–C(5)); 1.44 (*ddd*, *J* = 12.3, 7.9, 4.9, H_{exo}–C(6)); 1.28–1.23 (*m*, H_{endo}–C(5)); 0.94 (*s*, Me–C(1), Me_{syn}); 0.88 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 136.1 (*d*, *C*H=CH_2); 117.0 (*t*, CH=*C*H_2); 103.1

(*s*, C(2)); 81.4 (*d*, C(5′)); 54.0 (*s*, C(1)); 50.7 (*t*, C(3)); 48.1 (*s*, C(7)); 46.4 (*d*, C(4)); 39.3 (*t*, C(4′)); 30.2 (*t*, C(6)); 27.0 (*t*, C(5)); 21.0 (*q*, Me_{syn}); 20.2 (*q*, Me_{anti}); 12.4 (*q*, Me–C(1)). CI-MS (i-butane): 240 (14), 239 (67, $[M + H]^+$), 238 (24, $M^{+\bullet}$), 237 (12), 184 (11), 154 (17), 153 (100), 143 (18), 129 (19), 127 (8), 125 (11), 108 (7). CI-MS (NH_3): 240 (7), 239 (36, $[M + H]^+$), 238 (24), 171 (11), 170 (100), 108 (6).

Date of **11**: Colorless oil. $[\alpha]_D^{23} = -33.0$. IR: 3083*w*, 3016*w*, 2955*s*, 2885*m*, 1646*w*, 1481*m*, 1454*m*, 1389*m*, 1369*w*, 1306*w*, 1165*w*, 1110*m*, 1071*s*, 1050*m*, 1004*m*, 986*m*, 925*m*, 875*w*, 843*w*, 801*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.89 (*ddd*, *J* = 17.1, 10.6, 6.4, C*H*=CH_2); 5.31 (*dd*, *J* = 17.2, 1.3, 1 H of =CH_2); 5.14 (*dd*, *J* = 10.4, 1.4, 1 H of =CH_2); 4.52–4.49 (*m*, H–C(5′)); 2.94 (*dd*, *J* = 10.6, 4.5, 1 H–C(4′)); 2.71 (*t*-like, *J* ≈ 10.2, 1 H–C(4′)); 2.45 (*dt*-like, *J* ≈ 13.7, 4.1, H_{exo}–C(3)); 1.97 (*d*, *J* = 13.7, H_{endo}–C(3)); 1.73 (*t*, *J* = 4.5, H–C(4)); 1.69–1.66 (*m*, H_{exo}–C(5)); 1.57–1.46 (*m*, 2 H–C(6)); 1.20–1.15 (*m*, H_{endo}–C(5)); 1.05 (*s*, Me_{syn}); 0.92 (*s*, Me–C(1)); 0.86 (*s*, Me_{anti}). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 137.1 (*d*, *C*H=CH_2); 116.3 (*t*, CH=*C*H_2); 105.4 (*s*, C(2)); 85.4 (*d*, C(5′)); 54.8 (*s*, C(1)); 52.0 (*t*, C(3)); 48.6 (*s*, C(7)); 45.4 (*d*, C(4)); 37.6 (*t*, C(4′)); 33.3 (*t*, C(6)); 26.8 (*t*, C(5)); 21.2 (*q*, Me_{anti}); 20.7 (*q*, Me_{syn}); 10.4 (*q*, Me–C(1)). CI-MS (i-butane): 305 (16), 241 (9), 240 (25), 239 (93, $[M + H]^+$), 238 (52, $M^{+\bullet}$), 237 (22), 184 (13), 169 (11), 154 (15), 153 (100), 143 (23), 129 (29), 127 (12), 125 (16), 109 (10), 108 (13), 95 (7).

Treatment of **9** (100 mg, 0.42 mmol) with 1 equiv. of $ZnCl_2$ in THF (5 ml) under an N_2 atmosphere (2 h, reflux, PLC (hexane)) gave 47 mg (47%) of **10** and 36 mg (36%) of **11**, respectively.

5. *Epimerization of* **3** *to* **7***, and of* **10** *to* **11**. Irradiation of **3** in $CDCl_3$ (NMR tube) at r.t. with sunlight (16 h of irradiation, workup after 56 h) afforded a mixture of **3** and **7** in a ratio of 1 : 15. Treatment of **3** (100 mg, 0.42 mmol) with 1 equiv. of $ZnCl_2$ in THF (5 ml) under an N_2 atmosphere (45 min, reflux) and aq.

work-up gave **3** and **7** in a ratio of 1 : 1 according to ^{1}H-NMR. However, no epimerization of **3** to **7** took place when **3** was treated with 0.5 equiv. of $ZnCl_2$ in CH_2Cl_2 (5 ml) at – 20° for 26 h.

Treatment of **10** (100 mg, 0.42 mmol) in $CHCl_3$ (15 ml) at r.t. with 10 drops of conc. HCl (14 h, PLC (hexane)) yielded 42 mg (42%) of **11**, and 40 mg (40%) of the starting material **10** was recovered.

5. *Thio*-Claisen *Rearrangement of* **4**. Heating of a soln. of **4** (150 mg, 0.63 mmol) in mesitylene (15 ml) under an N_2 atmosphere to reflux (12 min, PLC (hexane/Et_2O 1: 1)) led to 132 mg (88%) of *(1*R*,3*S*,4*R*)-3-((2*Z*)-4′-hydroxybut-2′-en-1′-yl)-1,7,7-trimethylbicyclo[2.2.1]heptane-2-thione* (**12**). Pink orange oil. $[\alpha]_D^{23}$ = + 254.3. IR: 3345*m* (br., OH), 2960*s*, 2870*m*, 1669*w*, 1485*w*, 1444*m*, 1390*m*, 1375*m*, 1294*m*, 1267*m*, 1254*m*, 1231*w*, 1125*m*, 1099*m*, 999*m*, 970*m*, 832*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 5.73–5.71 (*m*, H–C(2′), H–C(3′)); 4.13–4.07 (*m*, 2 H–C(4′)); 2.98–2.93 (*m*, 1 H–C(1′)); 2.67–2.63 (*m*, H_{exo}–C(3)); 2.12 (*t*-like, $J \approx 4.1$, H–C(4)); 2.04–1.98 (*m*, 1 H–C(1′)); 1.83–1.71 (*m*, H_{exo}–C(5), 1 H–C(6)); 1.56–1.49 (*m*, H_{endo}–C(5), OH); 1.16–1.09 (*m*, 1 H–C(6)); 1.08 (*s*, Me–C(1)); 1.07 (*s*, Me_{anti}); 0.82 (*s*, Me_{syn}). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 274.8 (*s*, C=S); 130.5 (*d*, C(2′), C(3′)); 70.4 (*s*, C(1)); 63.6 (*t*, C(4′)); 60.0 (*d*, C(3)); 48.1 (*s*, C(7)); 47.6 (*d*, C(4)); 34.9 (*t*, C(6)); 34.1 (*t*, C(1′)); 20.3 (*t*, C(5)); 19.9 (*q*, Me_{anti}); 19.3 (*q*, Me_{syn}); 13.7 (*q*, Me–C(1)). CI-MS (i-butane): 238 (8, $M^{+\bullet}$), 223 (6), 222 (15), 221 (100, $[M - H_2O + H]^+$).

6. *[3,3]-Sigmatropic Rearrangement of Intermediate Xanthate* **13**. To a two-phase system of 50% aq. NaOH (2.2 ml) containing 61.2 mg (0.189 mmol) of *n*-Bu_4NHSO_4 and 2.2 ml of CS_2, **9** (450 mg, 1.89 mmol) and MeI (1.342 g, 9.45 mmol) were added. The mixture was vigorously stirred overnight at r.t. The CS_2 layer was separated, and the aq. layer was extracted 3× with CS_2. The combined org. layers were washed with H_2O, dried ($MgSO_4$), and filtered. Removing the

solvent *in vacuo* and drying the residue in high vacuum (48 h) gave 500 mg (80.6%) of pure *S-methyl S-(2*E*)-4-[(1*′R*,4*′R*)-(1′,7′,7′-trimethylbicyclo[2.2.1]hept-2′-en-2′-yl)sulfanyl]but-2-en-1-yl dithiocarbonate* (**14**). Yellow oil. $[\alpha]_D^{23}$ = – 28.5. IR: 2952*vs*, 2870*s*, 1647*vs*, 1560*m*, 1471*m*, 1452*m*, 1439*m*, 1385*m*, 1374*m*, 1364*m*, 1298*m*, 1253*w*, 1219*m*, 1186*w*, 1134*w*, 1105*w*, 1044*m*, 963*s*, 874*vs*, 820*w*, 780*m*, 714*m*. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.76–5.69 (*m*, H–C(3)); 5.67–5.62 (*m*, H–C(2)); 5.51 (*d*, *J* = 2.3, H–C(3′)); 3.62 (*d*, *J* = 6.2, 2 H–C(1)); 3.27 (*d*, *J* = 6.3, 2 H–C(4)); 2.43 (*s*, SMe); 2.42 (br. *s*, H–C(4′)); 1.90–1.81 (*m*, 1 H); 1.52–1.45 (*m*, 1 H); 1.09–0.91 (*m*, 2H); 0.98 (*s*, Me); 0.82 (*s*, Me); 0.78 (*s*, Me). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 189.3 (*s*, C=O); 143.1 (*s*, C(2′)); 129.5, 127.4 (2*d*, *C*H=*C*H); 125.5 (*d*, C(3′)); 56.5, 56.1 (2*s*, C(1′), C(7′)); 52.2 (*d*, C(4′)); 32.8, 32.3, 31.5, 26.5 (4*t*, 4 *C*H_2); 19.5, 19.4, 12.9, 11.1 (4*q*, 4 Me). CI-MS (NH_3): 331 (16), 330 (20), 329 (100, $[M + H]^+$), 169 (41).

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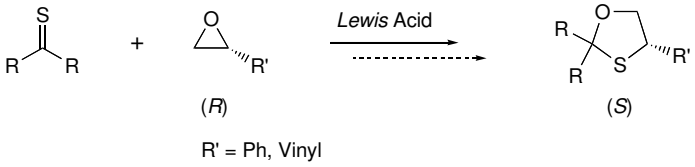
Table 1. *$SnCl_4$- and SiO_2-Catalyzed Reactions of* **1** *with* **2** *in CH_2Cl_2*

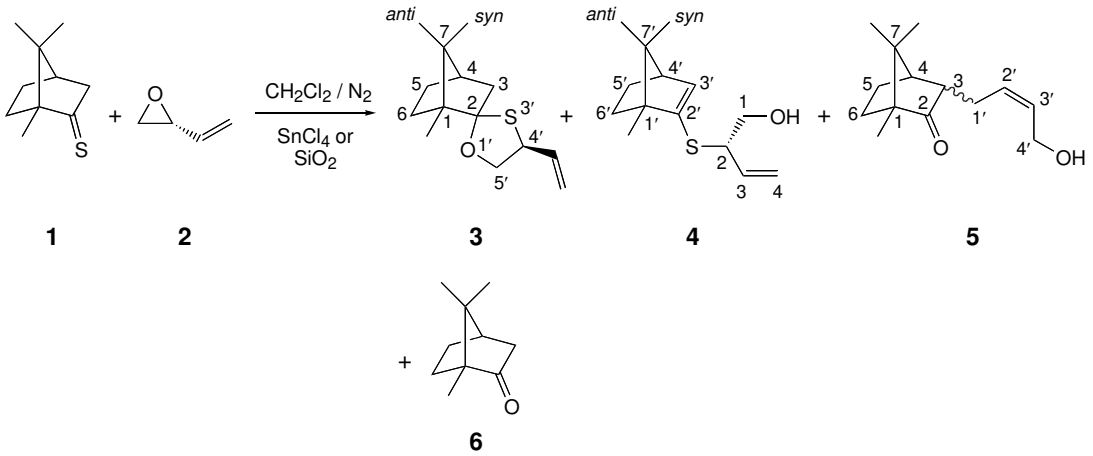
Lewis Acid	Temp. [°]	Reaction time	Yield of products [%]				
			3	**4**	**5**	**6**	**1**
$SnCl_4$	– 78	25 min	49	23	3	2	1
SiO_2	0	2 d	39	6	–	1	1

Scheme 1



R' = Ph, Vinyl

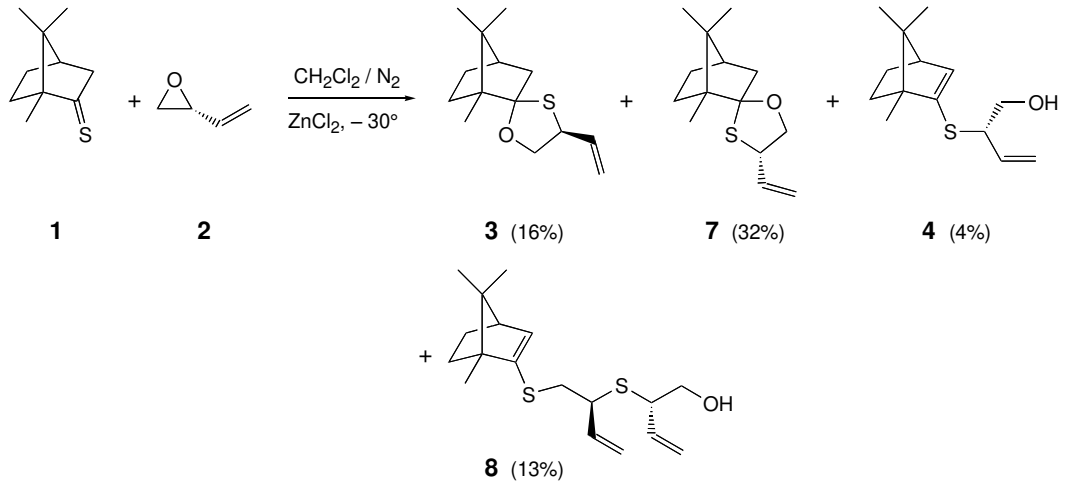
Scheme 2



1 **2** **3** **4** **5**

6

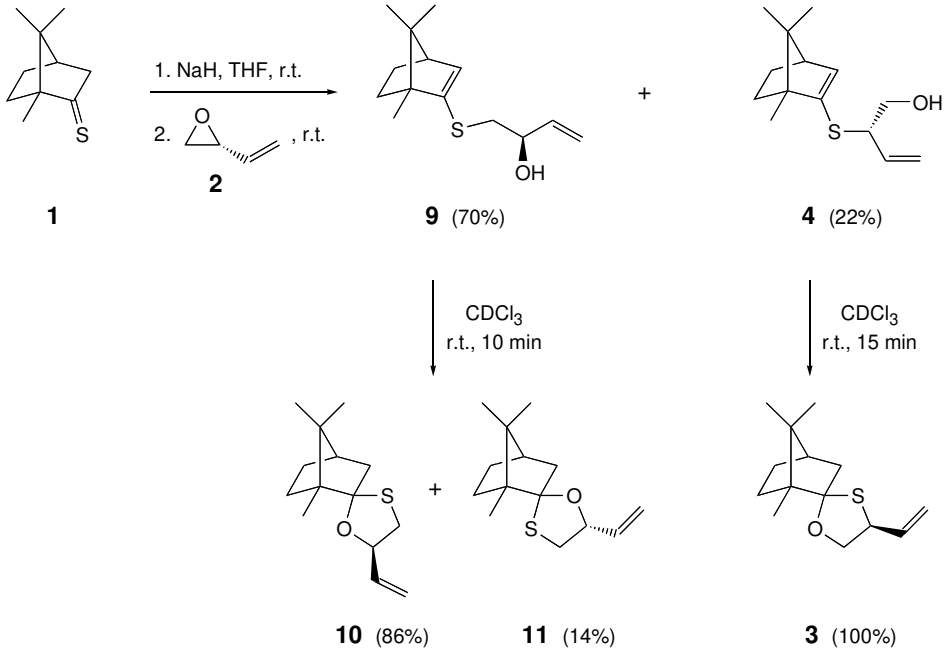
Scheme 3



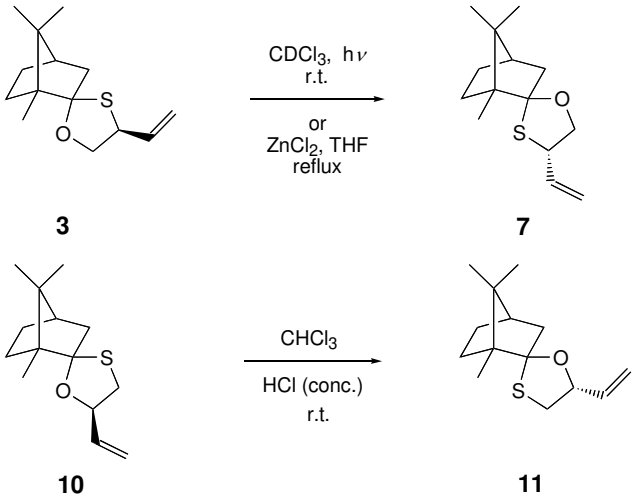
1 **2** **3** (16%) **7** (32%) **4** (4%)

8 (13%)

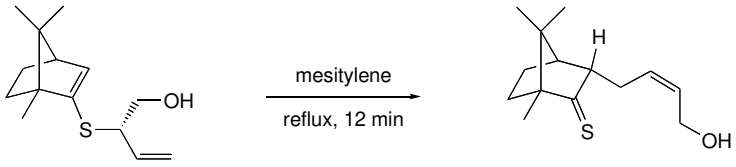
Scheme 4


1. NaH, THF, r.t.
2.
, r.t.
2
1
9 (70%)
4 (22%)
CDCl3
r.t., 10 min
CDCl3
r.t., 15 min
10 (86%)
11 (14%)
3 (100%)

Scheme 5

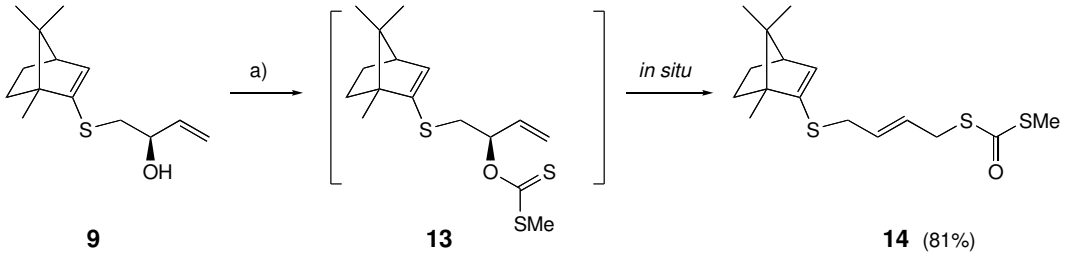

CDCl3, hν
r.t.
or
ZnCl2, THF
reflux
S
O
O
S
3
7
CHCl3
HCl (conc.)
r.t.
S
O
O
S
10
11

Scheme 6



4 **12** (88%)

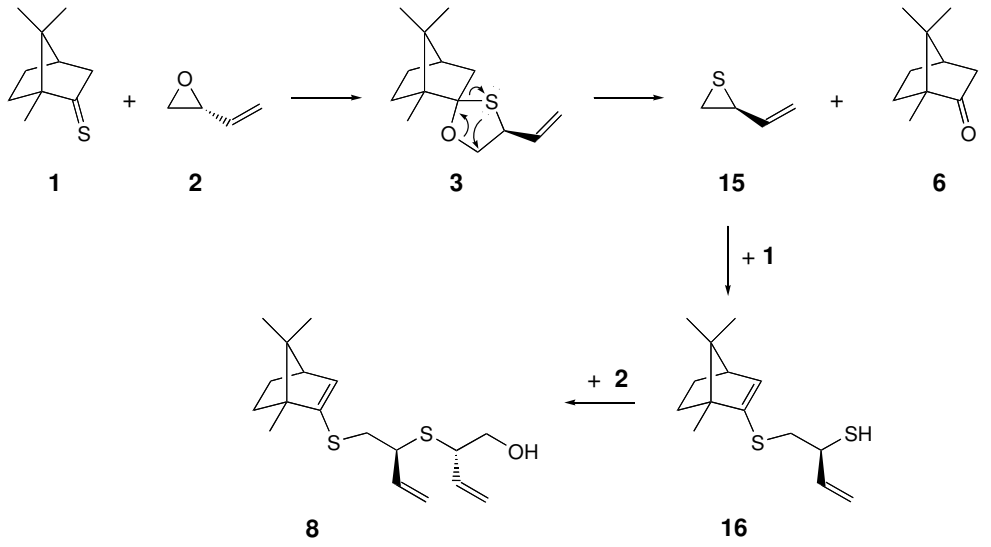
Scheme 7



9 **13** **14** (81%)

a) CS_2, MeI, NaOH, *n*-Bu_4NHSO_4, H_2O, r.t., overnight

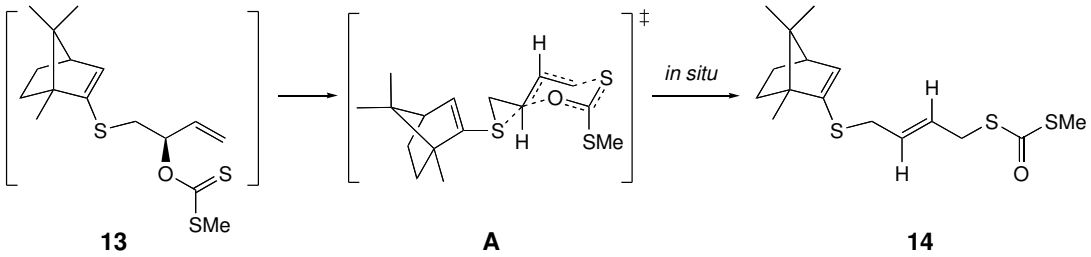
Scheme 8



1 **2** **3** **15** **6**

8 **16**

Scheme 9



13 **A** **14**

Scheme Graphical Abstract